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(19) (CA) # CANADIAN PATENT

(54) PROCESS FOR CARRYING OUT REACTIONS OF PARTIAL OXIDATION WITH OXYGEN OF ORGANIC COMPOUNDS IN VAPOUR PHASE AND APPARATUS SUITABLE TO CARRY OUT SAID PROCESS

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ABSTRACT OF THE DISCLOSURE:

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The present invention is concerned with a process for the partial oxidation with oxygen of organic compounds in vapour phase, characterized in that it comprises: feeding a mixture of the organic compound to be partially oxidized with oxygen or a gas containing oxygen, to a first zone containing an inert filling and wherein the gaseous mixture is heated to a temperature of from 100 to 300°C, reacting the heated mixture in a second zone which is contiguous to the first zone without solution of continuity and contains a catalytic filling and, then, cooling in a third zone the reaction products obtained to a temperature lower than 150°C, the third zone being contiguous or not to the second zone. The process of the invention enables to carry out the partial oxidation of organic compounds, in particular ethylene, with oxygen present in the fed mixture in an amount as high as 20% by volume. An apparatus is also disclosed for carrying out the above process.

The present invention relates to a process for the partial oxidation with oxygen of organic compounds in vapour phase and to an apparatus suitable to carry out such process.

More particularly, the invention relates to a process for the partial oxidation with O_2 of ethylene to ethylene oxide in vapour phase and to an apparatus suitable to carry out this oxidation.

For the sake of simplicity, reference will be made hereinafter exclusively to the partial oxidation with O_2 of ethylene to ethylene oxide even if the process and the apparatus therefor are suitable to carry out any partial oxidation.

The invention will be better understood with reference to the accompanying drawings, wherein:

Fig. 1 is a flow diagram of a know process for preparing ethylene oxide starting from ethylene and oxygen;

Fig. 2 is a schematic representation of a single reactor tube used for carrying out a process according to the present invention;

Fig. 3 is a flow diagram of a process according to the invention for the production of ethylene oxide;

Fig. 4 is a schematic representation of a reactor tube according to a further embodiment;

Fig. 5 is a flow diagram of the process according to a further embodiment; and

Fig. 6 is a partial flow diagram illustrating a further embodiment of the process according to the invention.

Referring to fig. 1, processes known in the art may be carried by means of a reactor 1 comprising a bundle of tubes containing the catalyst for the reaction. In order to remove the heat produced during the reaction, a heat exchange fluid is circulated by means of a pump 3 in the sheel of the reactor and is then cooled in a heat exchanger 2 to produce steam. This applies if the fluid is maintained in liquid state; however, if

use is made of an evaporating fluid, pump 3 may be eliminated since the fluid circulation can be effected by gravity flow. Water may be used as evaporating fluid and, in such a case, the heat exchanger 2 can be also eliminated as the steam is produced directly in the shell of reactor 1.

The gas leaving the reactor heats the gas fed to the same reactor by means of a heat exchanger 4; then, it is fed into column 5 wherein the ethylene oxide is absorbed by a suitable solvent 10, generally but not necessarily water. The gas after absorption of the oxide is recycled to the reactor by means of a compressor 6.

The fresh reagents, i.e., ethylene and the oxidizing agent (air or oxygen), are fed through conduits 7 and 8.

For avoiding an accumulation of the inert gases which enter together with the reagents, a small quantity of gas is vented through conduit 9. In the case of plants wherein air is used as oxidizing agent, the ethylene contained in the exhaust gases is fed to a subsidiary system analogous to the one described above; in the case of plants wherein use is made of oxygen, a carbon oxide absorption stage is inserted in the cycle.

Both heat exchangers 2 and 4 constitute essential parts of processes known in the art.

In fact, the production of steam in heat exchanger 2 is not a negligible feature of the plant economy since it can be exploited in the plant itself for producing energy or can be brought outside the battery limit; also, heat exchanger 4 has an essential function as to the recovery of heat which is exploited for heating the gas to be fed to the reactor.

It is to be noted however that the presence of the heat exchanger 4 causes the reagents fed to the reactor to remain at a high temperature during the time taken to flow through the section of pipe extending from the heat exchanger to the reactor inlet. This involves, as a consequence, that the O_2 content of the feed

mixture must be lower than the one corresponding to the flammability limit at that temperature, that is at most 7 to 8%.

Therefore, according to the art, the reaction mixture is fed to the reactor at the maximum possible temperature, after having been preheated, through a suitable heat exchanger, by the reaction mixture leaving the same reactor. As the reaction is being exothermic, it is thereby possible to produce the maximum amount of steam by exploiting the heat from the reaction. In accordance with this technique, it is only possible to operate, as aforesaid, with low oxygen concentrations in the mixture entering the reactor because of the possibility of explosion. Consequently, the concentration of the desired oxygen-containing compound in the mixture leaving the reactor is low and, therefore, big reactors are necessary; the gas must circulate at high flow rates and must be compressed and, furthermore, the system for recovering the oxygen-containing compound is also expensive.

It has now been found that the concentration of oxygen at the reactor inlet can be substantially increased and consequently all the aforesaid drawbacks reduced, by carrying out the heating of the mixture of ethylene and oxygen, wherein the latter is present in a high concentration, through heat exchange with a hot fluid in a zone which is adjacent to the reaction zone and upstream of the same. This heating zone comprises preferably a foundle of tubes containing a filling which is inert with respect to the reagents.

The process according to the present invention comprises feeding, at room temperature, a mixture of the ethylene to be partially oxidized, with oxygen or a gas containing oxygen, to a first zone containing an inert filling and wherein the gaseous mixture is heated to a temperature of from 180 to 220°C, reacting the heated mixture in a second zone which is contiguous to the heating zone without solution of continuity and contains a catalytic filling and, then, cooling in a third zone the reaction

products obtained to a temperature lower than 150°C, the cooling zone being contiguous or not to the reaction zone.

The concentration of oxygen in the fed mixture may be as high as 20% by volume and the cooling and heating being effected by heat exchange, the heat withdrawn from the cooling zone being utilized in the heating zone.

While the reaction zone, which preferably comprises a bundle of tubes, contains a catalytic filling, the cooling zone which may also consists of a bundle of tubes may contain or not an inert filling. In the case where the cooling zone is not contiguous to the reaction zone but, on the contrary, separated from the same, the filling is preferably absent.

The first, second and third zones can obviously be portions of the same bundle of tubes.

As to the inert filling, use may be made of inert solid materials having the shape of small cylinders, small balls, Rasching rings or of any other shape. The empty space present in the various zones is preferably lower than 50%.

In the case where the cooling and heating zones consist of a bundle of tubes, the ratio between the maximum dimension of one of the filling bodies and the internal diameter of the tubes must be less than 0.40 and preferably comprised between 0.30 and 0.006.

In figure 2, there is shown a single reactor tube used for carrying out the process of the invention; the heating of the reagents is effected in portion 12 while the reaction occurs in portion 4 and, in the portion 11, the reaction products are cooled.

Portions 11 and 12 are filled in general with an inert material while the catalyst is contained in portion 4.

With reference to figure 3, it is possible to see that ethylene 7 and oxygen 8 are fed through 13 into a reactor 1

consisting of a bundle of tubes according to fig. 2 but, before reacting, they are heated through zone 12 and cooled after the reaction through zone 11 by means of a fluid 18 which circulates between zones 11 and 12 by means of a pump 10.

The gases leaving the reactor through 14 are fed to a column 5 wherein the ethylene oxide is absorbed by a liquid 15. The gases not absorbed by the liquid leave column 5 as overhead product, which are in part discharged through 9 and in part recycled through 6 to the reactor together with the feed.

The heat produced during the reaction is removed by heat exchange with a fluid 16 circulating in the reactor shell by means of a pump 3, to produce steam 17 in an evaporator 2.

The heat from the reaction can be indifferently removed either by means of a circulating liquid or an evaporating liquid other than water or by water evaporating directly in the reactor shell.

In this way, it is possible to control easily the heat development and the course of the reaction.

A further object of the present invention is an apparatus by means of which the process preceedingly described can be carried out.

The apparatus according to the invention is characterized by the combination of: a reactor including a shell and a bundle of tubes within the shell; means dividing the bundle of tubes into an intermediate and two end zones; means for cooling the intermediate zone and one of the end zones, including means to convey the heat withdrawn from this end zone to the other end zone so as to heat this latter zone; a catalyst filling the tubes of the intermediate zone; and an inert solid material filling the tubes of the end zone which heated.

According to a preferred embodiment, the tubes of the end zone which is cooled are filled with an inert solid material.

According to a further embodiment, the means for cooling the intermediate zone includes an evaporating fluid.

Referring again to fig. 3, the apparatus consists of a reactor 1 comprising a bundle of tuber which are connected at their ends to two plates 19 and 20 to which are joined respectively

the top 21 and bottom 22 of the reactor by flanging or welding. The tubes are filled for a sufficient length at both ends with an inert solid material and, in the intermediate portion, they are filled with a catalyst, the catalyst and the inert material being of suitable shape, such as small cylinders, small balls or Rasching rings.

The bundle of tubes is covered by a shell and is divided on the shell side by 2 baffles 23 and 24 into 3 distinct portions 12, 4 and 11 wherein respectively heating of the reagents, reaction and cooling of the reaction products occur.

In the tubular section 11, the filling can be also absent.

The apparatus is completed by a circuit 18 along which a liquid circulates for heating section 12 and cooling section 11. The circulation is achieved by means of a pump 10.

There is also provided a circuit 16 for cooling section 4 of the reactor; the fluid circulating in the circuit removes the heat from the reaction zone 4 and utilizes it in evaporator 2 to produce zone 17. The circulation in circuit 16 is achieved by means of a pump 3.

As aforesaid, use may be made in circuit 16 of a liquid which may be an evaporating liquid and, in this case, both pump 3 and evaporator 2 are eliminated.

Fig. 4 illustrates schematically a single tube of the reactor 1 according to fig. 5. As seen, this reactor tube comprises a section 12 containing an inert filling and wherein the gases are heated and a section 4 containing a catalytic filling and wherein the reaction occurs.

In fig. 5, there is shown a modification of the diagram according to fig. 3, the variant being a heat exchanger 11 which is external to the reactor 1 and which may contain or not an inert filling. This heat exchanger has the same function as the cooling zone 11 of the reaction 1 according to fig. 3.

Finally, in fig. 6, there is shown a further embodiment of the reactor 1 which, in this case, comprises 4 heating zones and 4 cooling zones, there being a pump associated with each cooling and heating zone. An example will now be given for illustrating the subject invention, without limiting the scope thereof.

EXAMPLE

To a reactor like the one represented in figure 3, were fed at different times 3 mixtures. The composition of the fed mixtures, the reaction conditions and the results obtained are reported in the following Table.

Feed mixture	1st mixture	2nd mixture	3rd mixture
Ethylene	20% by volume	22% by volume	22% by volume
Oxygen	8 "	15 "	18 "
Carbon dioxide	10 "	10 "	10 "
Nitrogen	37 "	32 "	30.2 "
Argon	25 "	21 "	19.8 "
Reaction temperature (°C)	235	235	235
Temperature at the reactor inlet (°C)	180	45	45
Pressure at the reactor inlet (ata)	20	22	22
Concentration of ethylene oxide at the exit of the reactor	2.8%	5.2%	6.9%

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the partial oxidation with oxygen of ethylene in vapour phase, characterized in that it comprises:

a) feeding at room temperature a mixture of the ethylene to be partially oxidized with oxygen or a gaz containing oxygen, the concentration of oxygen in the mixture being less than 20% in volume, to a first zone containing an inert filling and wherein the gaseous mixture is heated to a temperature of from 180 to 220°C,

b) reacting the heated mixture in a second zone which is contiguous to said first zone without solution of continuity and contains a catalytic filling, and

c) cooling in a third zone the reaction products obtained to a temperature lower than 150°C, said third zone being contiguous or not to said second zone, the cooling and heating being effected by heat exchange, the heat withdrawn from the cooling zone being utilized in the heating zone.

2. Process according to claim 1, wherein said third zone contains an inert filling.

3. Process according to claims 1 or 2, wherein use is made of inert solid materials having the shape of small cylinders, as inert filling.

4. Process according to claims 1 or 2, wherein use is made of inert solid materials having the shape of small balls, as inert filling.

5. Process according to claims 1 or 2, wherein use is

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made of inert solid materials having the shape of Rasching rings, as inert filling.

6. Process according to claim 1, wherein said first zone consists of a bundle of tubes.

7. Process according to claim 1, wherein said second zone consists of a bundle of tubes.

8. Process according to claim 1, wherein said third zone consists of a bundle of tubes.

9. Process according to claims 6, 7 and 8, wherein the first, second and third zone are portions of the same bundle of tubes.

10. Process according to claims 1 or 2, wherein said first and second zones consist respectively of a bundle of tubes filled with inert solid materials, the ratio between the maximum dimension of one of the inert filling materials and the internal diameter of the tubes being less than 0.40.

11. Process according to claims 1 or 2, wherein said first and second zones consist respectively of a bundle of tubes filled with inert solid materials, the ratio between the maximum dimension of one of the inert filling materials and the internal diameter of the tubes being comprised between 0.06 and 0.36.

12. An apparatus for carrying out a process for the partial oxydation with oxygen of organic compounds in vapour phase, characterized by the combination of:

- a reactor including a shell and a bundle of tubes within said shell;

- means dividing said bundle of tubes into an interme-

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diate and two end zones;

- means for cooling the intermediate zone and one of the end zones, including means to convey the heat withdrawn from said one end zone to the other end zone to heat the said other end zone;

- a catalyst filling the tubes of said intermediate zone; and

- an inert solid material filling the tubes of said other end zone.

13. Apparatus according to claim 12, wherein the tubes of said one end zone are filled with an inert solid material.

14. Apparatus according to claims 12 or 13, wherein said means for cooling the intermediate zone includes an evaporating fluid.

FIG. 1 (PRIOR ART)

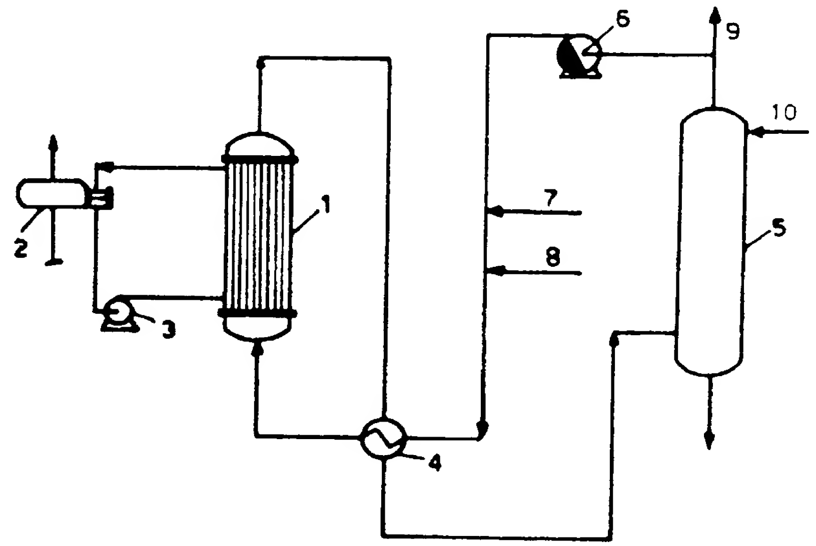
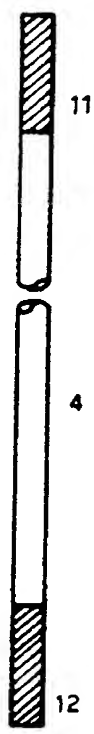


FIG. 2



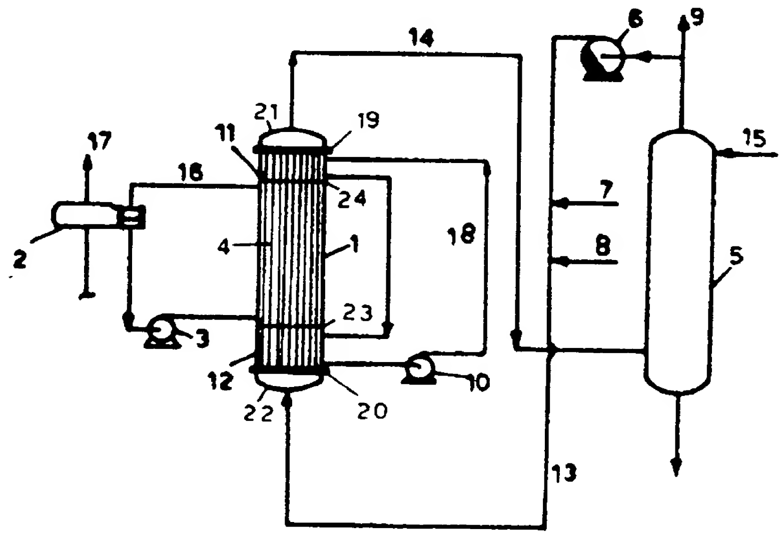


FIG. 3

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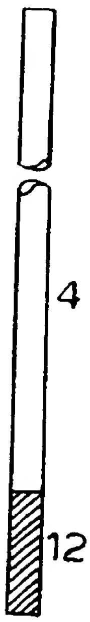
FIG. 4



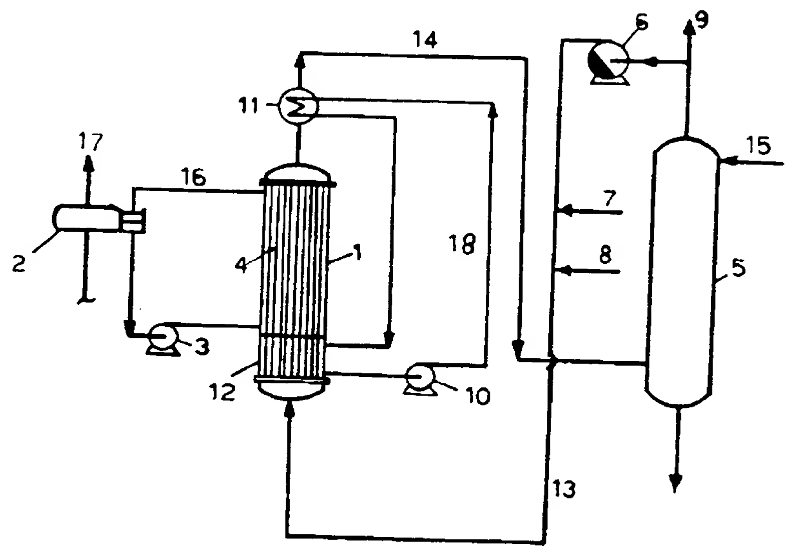


FIG. 5

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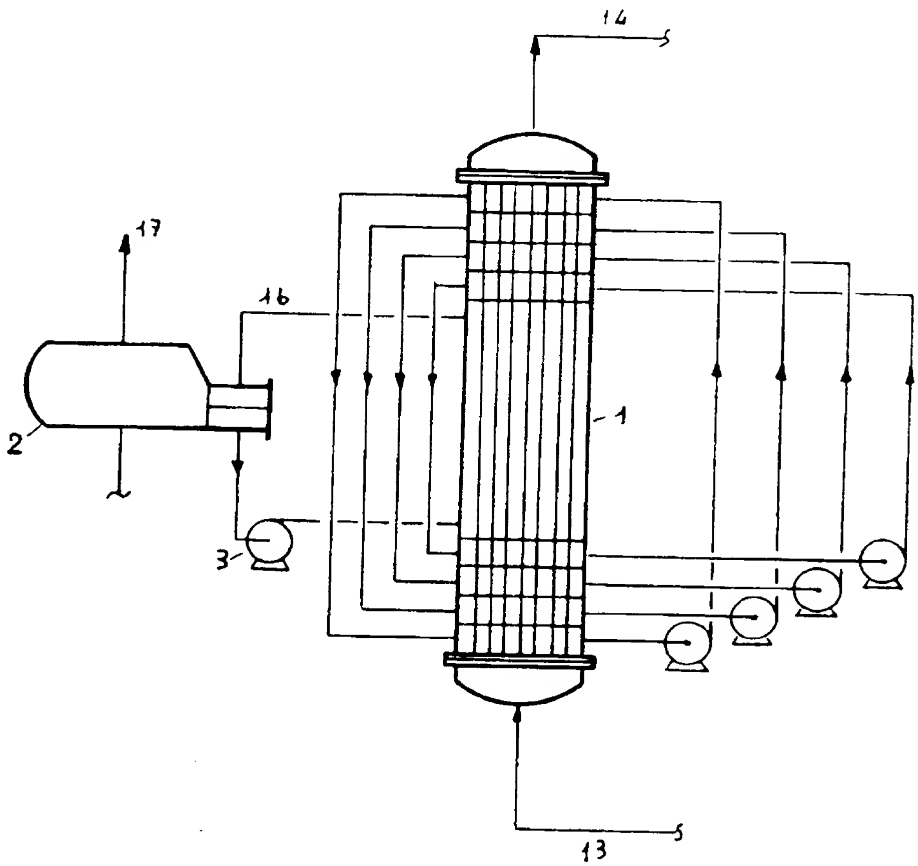

FIG.6

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